# Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean

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[1] Based on measurements from the WOCE/JGOFS global $CO_2$ survey, the CLIVAR/$CO_2$ Repeat Hydrography Program and the Canadian Line P survey, we have observed an average decrease of 0.34% $yr^{-1}$ in the saturation state of surface seawater in the Pacific Ocean with respect to aragonite and calcite. The upward migrations of the aragonite and calcite saturation horizons, averaging about 1 to 2 m $yr^{-1}$, are the direct result of the uptake of anthropogenic $CO_2$ by the oceans and regional changes in circulation and biogeochemical processes. The shoaling of the saturation horizon is regionally variable, with more rapid shoaling in the South Pacific where there is a larger uptake of anthropogenic $CO_2$. In some locations, particularly in the North Pacific Subtropical Gyre and in the California Current, the decadal changes in circulation can be the dominant factor in controlling the migration of the saturation horizon. If $CO_2$ emissions continue as projected over the rest of this century, the resulting changes in the marine carbonate system would mean that many coral reef systems in the Pacific would no longer be able to sustain a sufficiently high rate of calcification to maintain the viability of these ecosystems as a whole, and these changes perhaps could seriously impact the thousands of marine species that depend on them for survival.

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## 1. Introduction

[2] Carbon dioxide is one of the most important of the "green-house" gases in the atmosphere, contributing to the heat balance of the earth as well as affecting the calcium carbonate ($CaCO_3$) equilibrium in the oceans. As a result of the industrial and agricultural activities of humans since the beginning of the industrial era, atmospheric $CO_2$ concentrations have increased about 40% [*Prentice et al.*, 2001;

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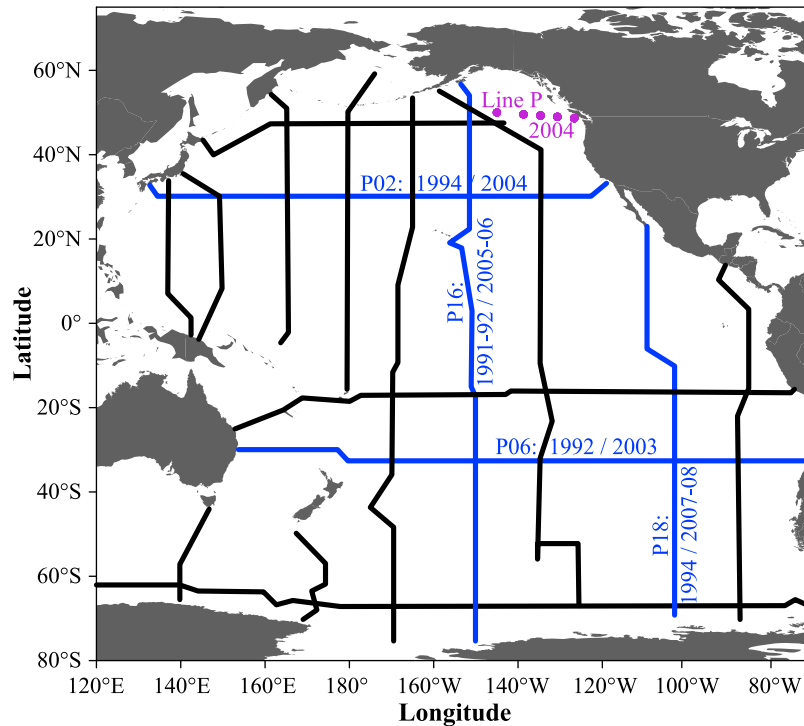[4]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA.
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*Royal Society*, 2005; *Solomon et al.*, 2007; *Sabine and Feely*, 2007]. Atmospheric $CO_2$ concentrations are now higher than has been experienced for at least the last 800,000 years [*Keeling and Whorf*, 2004; *Lüthi et al.*, 2008]. The global oceans are the largest natural long-term reservoir for the excess $CO_2$, currently absorbing 26% of the combined carbon released from deforestation and fossil fuel combustion up to the present and could absorb as much as 90% of the excess $CO_2$ over the next several millennia [*Archer et al.*, 1998; *Canadell et al.*, 2007; *Le Quéré et al.*, 2009; *Sabine et al.*, 2011]. Seawater chemistry is now changing in response to continually rising atmospheric $CO_2$ levels. For example, the mean surface ocean pH has decreased by about 0.1 units since the beginning of the industrial revolution [*Caldeira and Wickett*, 2003, 2005; *Feely et al.*, 2004, 2009a; *Orr et al.*, 2005]. If current carbon dioxide emission trends continue this process, commonly known as "ocean acidification," will occur at rates and extents that have not been observed for tens of millions of years [*Feely et al.*, 2004, 2009a; *Kump et al.*, 2009]. A doubling of atmospheric carbon dioxide concentration from pre-industrial levels, which could occur in as little as 50 years, is predicted to correspond with an average sea surface pH decrease of about 0.25 [*Caldeira and Wickett*, 2005].

[3] A growing number of research studies have demonstrated that under increasing ocean acidification conditions
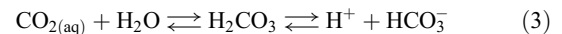
**Figure 1.** Map of the cruise sections used in this study from the international WOCE/JGOFS/OACES Global $CO_2$ Survey, the CLIVAR/$CO_2$ Repeat Hydrography survey lines and the Line P stations in the Pacific Ocean.

many marine $CaCO_3$-secreting species will soon be suffering adverse impacts. For example, the rate at which reef-building corals make their skeletons has been shown to decrease under increasing ocean acidification [*Gattuso et al.*, 1998; *Marubini and Atkinson*, 1999; *Marubini and Thake*, 1999; *Ohde and Van Woesik*, 1999; *Langdon et al.*, 2000, 2003; *Leclercq et al.*, 2000, 2002; *Marubini et al.*, 2003; *Guinotte et al.*, 2003; *Ohde and Hossain*, 2004; *Langdon and Atkinson*, 2005; *Silverman et al.*, 2007, 2009; *Anthony et al.*, 2008]. These reduced growth rates could make many reef ecosystems unsuitable for calcification by the end of this century. Similar decreases in the calcification rates of planktonic coccolithophores and foraminifera have been observed when the organisms were subjected to $CO_2$-enriched waters [*Spero et al.*, 1997; *Riebesell et al.*, 2000; *Zondervan et al.*, 2001, 2002; *Sciandra et al.*, 2003; *Seibel and Fabry*, 2003; *Riebesell*, 2004; *Delille et al.*, 2005; *Engel et al.*, 2005; *Fabry et al.*, 2008; *Guinotte and Fabry*, 2008; *Doney et al.*, 2009; *Riebesell and Tortell*, 2011]. Most of these studies have demonstrated a close positive correlation between the rate of marine calcification and the aragonite/calcite saturation state of seawater. Saturation state with respect to aragonite and calcite carbonate minerals is calculated as the product of the concentrations of $Ca^{2+}$ and $CO_3^{2-}$ divided by the apparent (i.e., relevant to seawater conditions) stoichiometric solubility product:

$$\Omega arag = \left[ Ca^{+2} \right]\left[ CO_3^{-2} \right]/Ksp{*}arag \qquad (1)$$

$$\Omega cal = \left[ Ca^{+2} \right]\left[ CO_3^{-2} \right]/Ksp{*}cal \qquad (2)$$

where $\Omega arag$ and $\Omega cal$ are calculated using the CO2SYS program developed by *Lewis and Wallace* [1998]. As atmospheric $pCO_2$ increases and equilibrates with seawater, carbonate ion is consumed via a series of reactions:

$$CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad (3)$$

$$and\ H^+ + CO_3^{-2} \rightleftarrows HCO_3^- \qquad (4)$$

where the reaction of $CO_{2(aq)}$ with $H_2O$ (3) leads to an initial increase in dissolved $H_2CO_3$ from the gas exchange process. These reactions are reversible and the thermodynamics of these reactions in seawater are well established [*Millero et al.*, 2002, and references therein]. It is these reactions in combination with the slow circulation and primary production throughout the global oceans that control pH over timescales of hundreds to thousands of years. By the end of this century, ocean acidification could decrease surface ocean pH by as much as 0.4 pH units relative to pre-industrial values [*Orr et al.*, 2005; *Meehl et al.*, 2007; *Joos et al.*, 2011]. The corresponding carbonate ion decrease in the surface waters would be approximately 50% [*Kleypas et al.*, 2006; *Feely et al.*, 2009b]. Thus, an increase in $pCO_2$ and a corresponding reduction in $CO_3^{2-}$ concentration will result in a reduction of saturation state with respect to $CaCO_3$ phases. In this paper, we document the decreases in the aragonite and calcite saturation state of the Pacific Ocean between the time of the WOCE/JGOFS Global $CO_2$ Survey and CLIVAR/$CO_2$ Repeat Hydrography Program. We will show how the changes in saturation state are affected by both the influx of anthropogenic $CO_2$ as well as
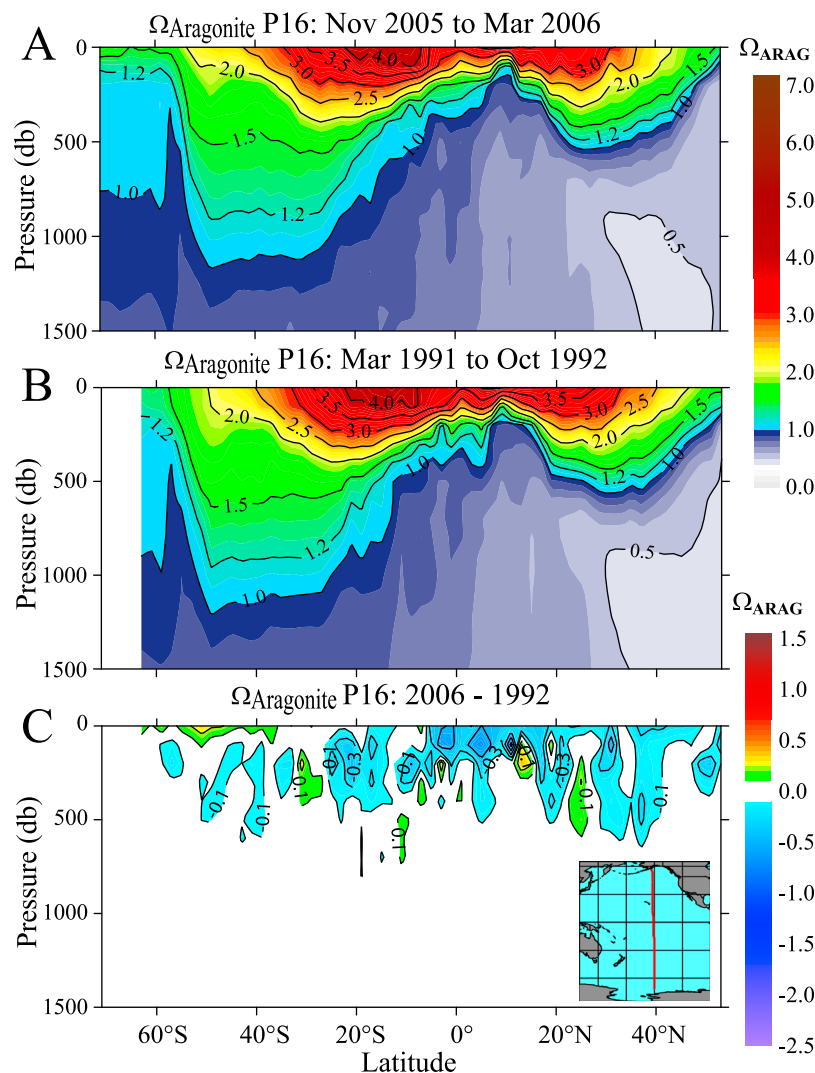
**Figure 2.** Aragonite saturation state for (a) ($\Omega$arag) for 2005/06, (b) 1991/02, and (c) $\Omega$arag difference (2005/06–1991/02) along the P16 section from Antarctica to Alaska.

changes in overturning circulation over the time interval between the observations.

## 2. The Data Sets

### 2.1. WOCE/JGOFS Global $CO_2$ Survey

[4] Carbon system measurements were made on 26 WOCE/JGOFS Global $CO_2$ Survey cruises between 1991 and 1996 in the Pacific Ocean [*Feely et al.*, 2004; *Sabine et al.*, 2004]. Dissolved inorganic carbon (DIC) was analyzed on all cruises using a coulometric titration [*U.S. Department of Energy (DOE)*, 1994; *Johnson and Wallace*, 1992; *Johnson et al.*, 1985, 1987; *Ono et al.*, 1998]. Total alkalinity [*DOE*, 1994; *Millero et al.*, 1993; *Ono et al.*, 1998] was the most common second carbon parameter on the cruises. However, on the P16N cruise, pH was measured as the second parameter [*Feely et al.*, 2009c; *Byrne et al.*, 2010]. Total alkalinity (TA) was calculated for these cruises using the *Mehrbach et al.* [1973] carbonate constants as refit by *Dickson and Millero* [1987]. The overall accuracy of the DIC data was ~3 $\mu$mol kg$^{-1}$ and ~5 $\mu$mol kg$^{-1}$ for the TA data [*Lamb*

*et al.*, 2002]. The final Pacific data set, containing about 35,000 sample locations with DIC and TA values, has been described in detail [*Key et al.*, 2004; *Sabine et al.*, 2005]. Both the WOCE/JGOFS Global $CO_2$ data set and the CLIVAR/$CO_2$ Repeat Hydrography data set are available from the CLIVAR and Carbon Hydrographic Data Office (http://whpo.ucsd.edu/) and the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/home.html).

### 2.2. CLIVAR/$CO_2$ Repeat Hydrography Data

[5] For the CLIVAR/$CO_2$ Repeat Hydrography cruises, samples were collected and analyzed for DIC, TA, oxygen, nutrient, tracer, and hydrographic data at repeat sections along the P02 (from Japan to the United States along 30°N; 2004), P16S (152°W from Tahiti to 71°S; 2005), P16N (along 152°W from Tahiti to Alaska; 2006), P6 (along 30°S from Australia to Chile; 2003), and P18 (along 110°W; 2007–2008 and 1994) transects (Figure 1). As a minimum, DIC and TA were measured on all the cruises. The CLIVAR/$CO_2$ data quality was confirmed by daily analyses of Certified Reference Materials [*Dickson*, 2001; *Dickson et al.*,
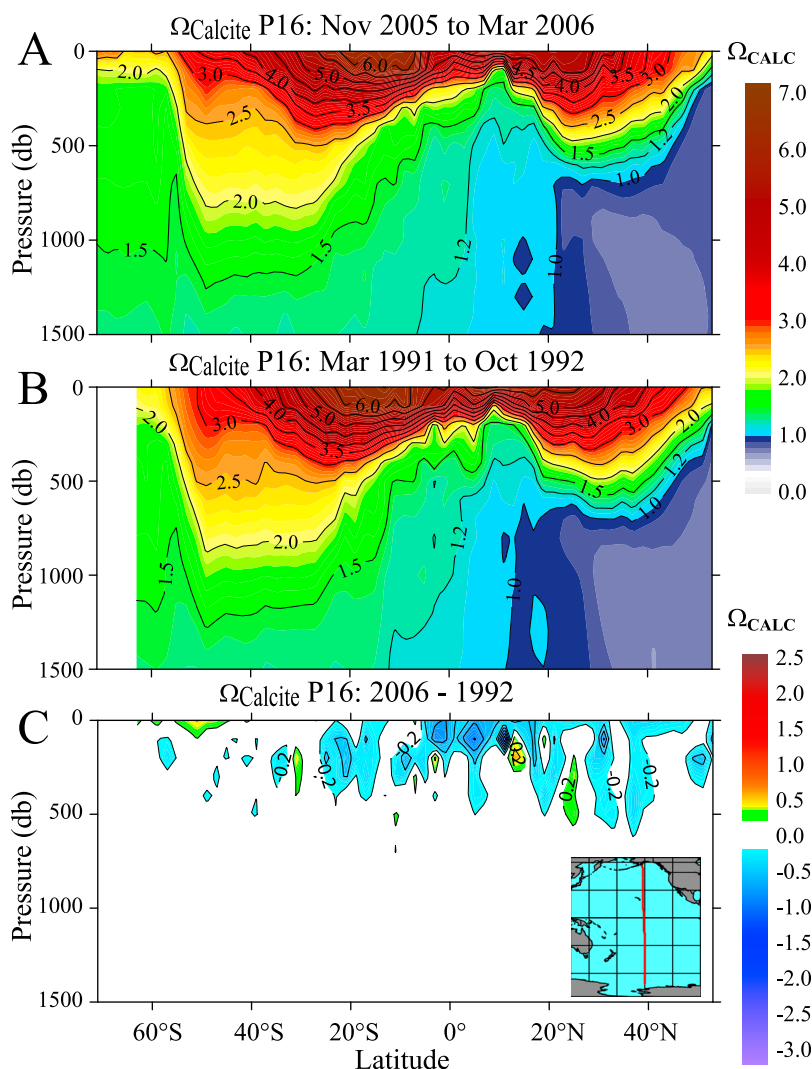
**Figure 3.** Calcite saturation state ($\Omega cal$) for (a) 2005/06, (b) 1991/02, and (c) $\Omega cal$ difference (2005/06 – 1991/02) along the P16 section from Antarctica to Alaska.

2007]. The consistency of the individual cruises was checked by comparing deepwater (>2000 m) values at stations that overlapped on P16S and P16N, and at the intersection of P16N and P02 [*Sabine et al.*, 2008]. These quality checks suggest that the DIC data are accurate within ~1 $\mu$mol kg$^{-1}$ and the TA data are accurate within ~3 $\mu$mol kg$^{-1}$. The P16 pH measurements were made spectrophotometrically with an overall precision of ±0.0015 [*Byrne et al.*, 2010]. The CLIVAR/CO$_2$ Repeat Hydrography physical and chemical data were compared to the 1990s WOCE/JGOFS data along the two P16N and P02 sections by examining values on isopycnal surfaces in deep water. The only observed offsets were found in the 1994 P02 TA data that required an adjustment of +10 $\mu$mol kg$^{-1}$.

### 2.3. Line P

[6] For the 2004 February Line P data [*Miller et al.*, 2009], samples were collected and analyzed for DIC, TA, oxygen, nutrient, and hydrographic data along Line P (Figure 1). DIC and TA were measured employing the CLIVAR/CO$_2$ methodology (Section 2.1 above), and were

confirmed by daily analyses of Certified Reference Materials and secondary standards directly calibrated against the certified materials [*Dickson*, 2001; *Dickson et al.*, 2007]. The consistency of the data were checked by comparing deepwater (>2000 m) values at stations that were close to the P16N section. These quality checks suggest that the DIC data are accurate within ~2 $\mu$mol kg$^{-1}$ and the TA data are accurate within ~3 $\mu$mol kg$^{-1}$.

### 3. Data Analysis

#### 3.1. Total Change in Aragonite/Calcite Saturation State Between Cruises

[7] Total changes in aragonite and calcite saturation levels were calculated using the CO2SYS program developed by *Lewis and Wallace* [1998]. The in situ degree of seawater saturation with respect to aragonite and calcite calculated from equations (1) and (2), where the Ca$^{+2}$ concentrations are estimated from salinity and carbonate ion concentrations, are calculated from the dissolved inorganic carbon (DIC) and total alkalinity (TA) data. The pressure effect on the
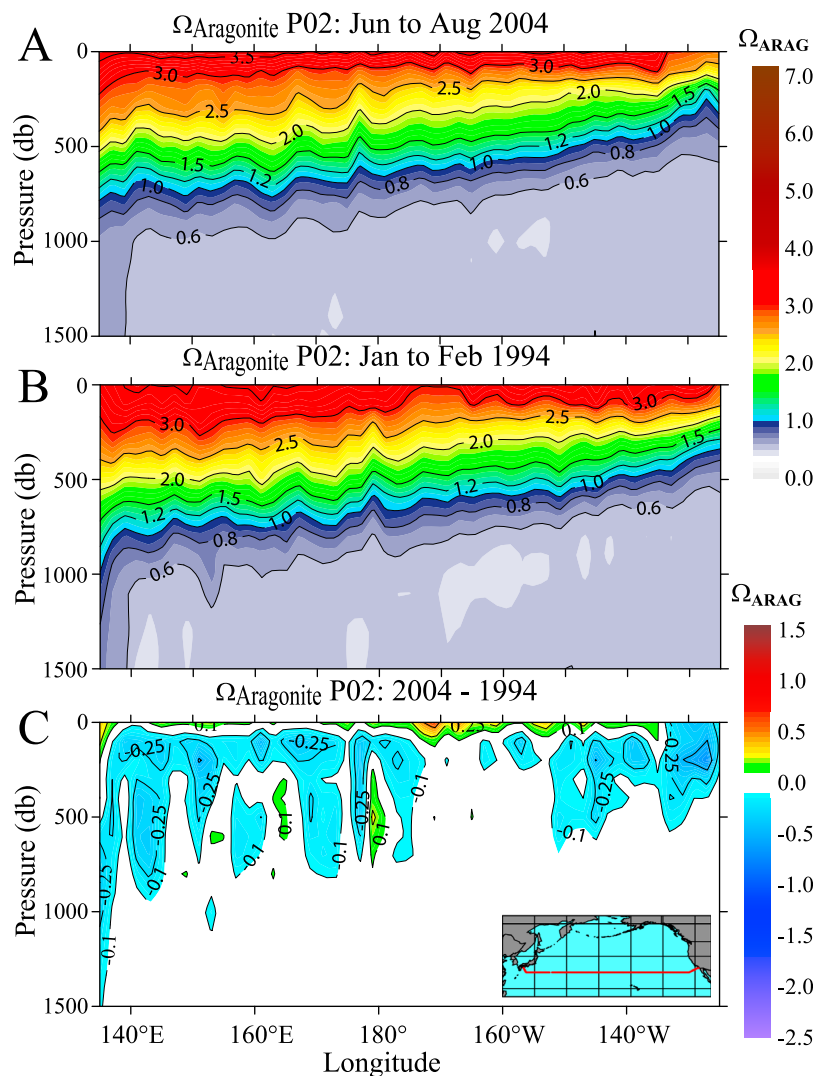
**Figure 4.** Aragonite saturation state for (a) (Ωarag) for 2004, (b) 1994, and (c) Ωarag difference (2004–1994) along the P02 section from Japan to Mexico.

solubility is estimated from the equation of *Mucci* [1983] that includes the adjustments to the constants recommended by *Millero* [1995]. The overall uncertainties of aragonite and calcite saturation state are on the order of $\pm0.03$ and $\pm0.05$, respectively. The aragonite solubility calculations are in agreement with field experiments of the first instance of aragonite dissolution based on freshly collected pteropod shells placed into a spectrophotometer under conditions of ambient temperature and pressure [*Feely et al.*, 1988]. The total changes in aragonite or calcite saturation state were calculated as the gridded and interpolated differences between saturation values estimated for each pair of repeat cruises.

## 3.2. Changes in Aragonite/Calcite Saturation State Due to Changes in Anthropogenic $CO_2$ and Changes in Circulation and Mixing Processes

[8] The extended multiple linear regression (e-MLR) approach developed by *Friis et al.* [2005] was used for this analysis. In this procedure, the observed DIC and TA data are fitted as a function of physical (e.g., temperature, salinity) and chemical (e.g., phosphate, nitrate, silicate) parameters. Multiple linear regression fits are determined for each cruise using the same set of independent physical and chemical parameters [*Sabine et al.*, 2008]. The coefficients of these two fits are then subtracted, such that the resulting equation directly determines the net DIC and TA change between the two cruises. Using this method, much of the random variability in the independent parameter measurements is minimized for both cruises, and the propagation of errors that results from a particular independent parameter's inability to describe completely the dependent parameter are partially canceled out when the coefficients are subtracted [*Friis et al.*, 2005; *Sabine et al.*, 2008; *Wanninkhof et al.*, 2010; *Goodkin et al.*, 2011]. The determination of which parameters are selected for use is based on the statistical fits of the field data. Almost all studies to date have used salinity (S) and potential temperature ($\theta$) to characterize the conservative characteristics. For our study, all repeat cruises were fit as a function of: S, $\theta$, potential density, phosphate (P) and silicate (Si). Oxygen, or apparent oxygen utilization (AOU), was specifically not used for the fit in anticipation of
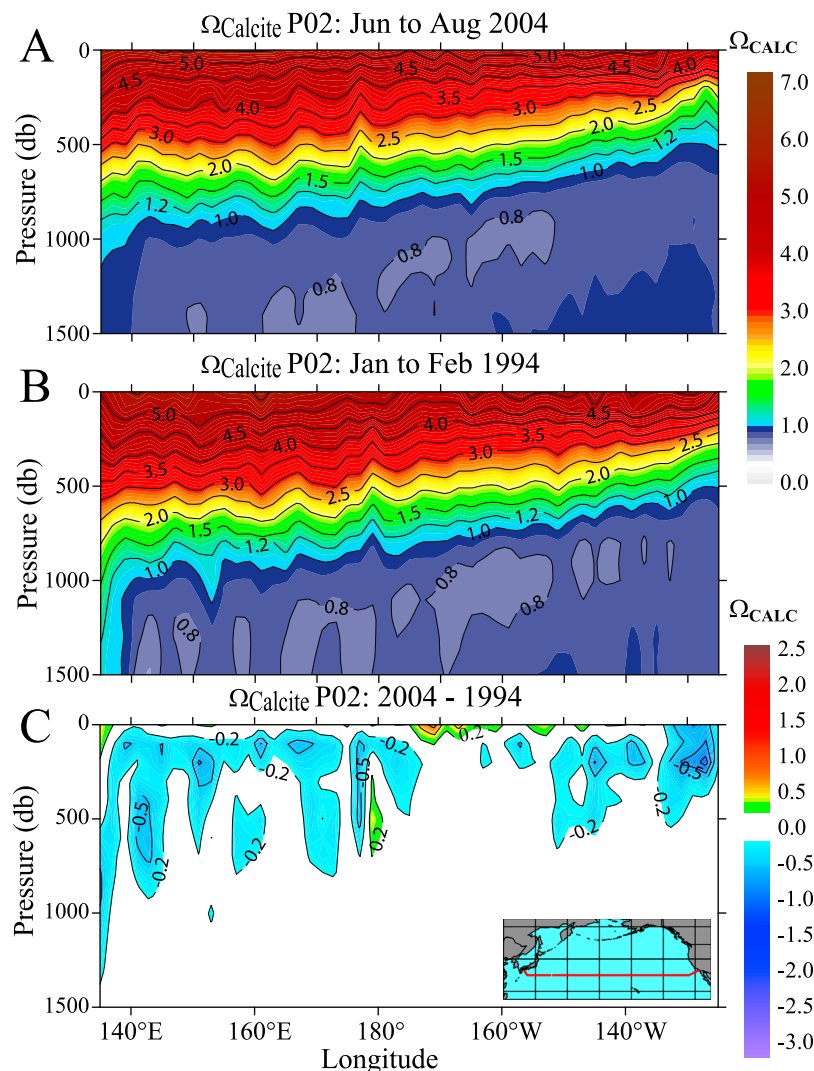
**Figure 5.** Calcite saturation state for (a) ($\Omega$cal) for 2004, (b) 1994, and (c) $\Omega$cal difference (2004–1994) along the P02 from Japan to Mexico.

using AOU to characterize the difference in the circulation changes as described below. The P16 and P02 lines were subdivided into three segments and fit with three independent e-MLR functions [*Sabine et al.*, 2008]. The divisions were chosen by first fitting all of the data along a section with a single function and plotting the residuals as a function of latitude (P16 and P18) or longitude (P02). The residuals resulted in a pattern, which indicated that the tropical Pacific (15°S–15°N) had a different pattern of residuals, and that of P02 should be divided at 145°E and 140°W. To estimate the circulation effects, AOU was fit using the same e-MLR approach that was applied to the carbon data. The coefficients and standard errors for the AOU fits are given by *Sabine et al.* [2008], employing a carbon to oxygen stoichiometric ratio of 117/170 [*Anderson and Sarmiento*, 1994]. *Sabine et al.* [2008] determined that approximately 80% of the DIC change in the North Pacific over the last decade is the result of circulation/ventilation changes and that circulation effects resulted in almost no change in the South Pacific [*Sabine et al.*, 2008, Figure 2]. The central core of the maximum AOU change appears to be associated

with the 26.6 potential density surface in the subtropical North Pacific, consistent with previous studies [*Emerson et al.*, 2001; *Ono et al.*, 2001; *Deutsch et al.*, 2006]. The change in aragonite/calcite saturation state that is due to the uptake of anthropogenic $CO_2$ is then determined by subtracting this circulation and/or ventilation change in DIC from the total change in DIC and getting the anthropogenic $CO_2$ change by difference. These new values are then used to estimate the change in saturation state that is due to the anthropogenic component. The technique is based on the assumption of constancy of the processes controlling the coefficients in the e-MLR equations. Significant changes in elemental ratios over time could lead to an underestimation of anthropogenic $CO_2$ contribution [*Wanninkhof et al.*, 2010].

## 4. Results

### 4.1. The P16 South-North Transects (2005–06 Versus 1991)

[9] There is significant shoaling of the aragonite and calcite saturation horizons from south to north in the Pacific
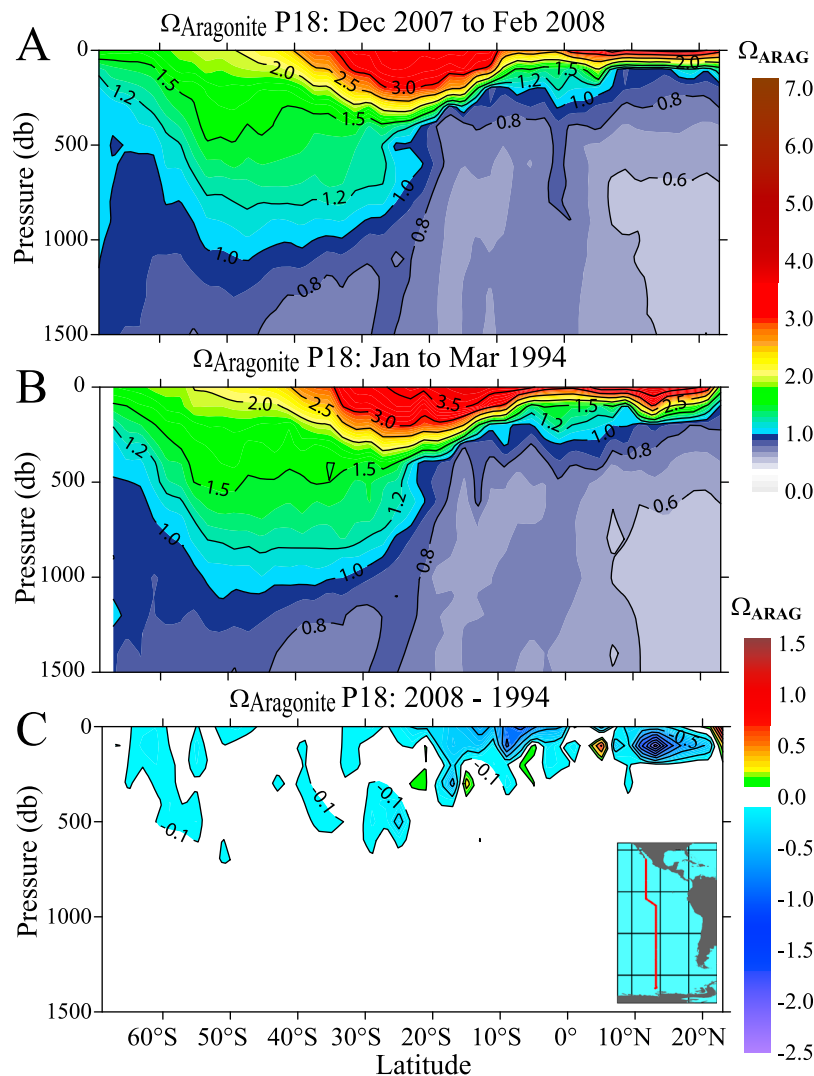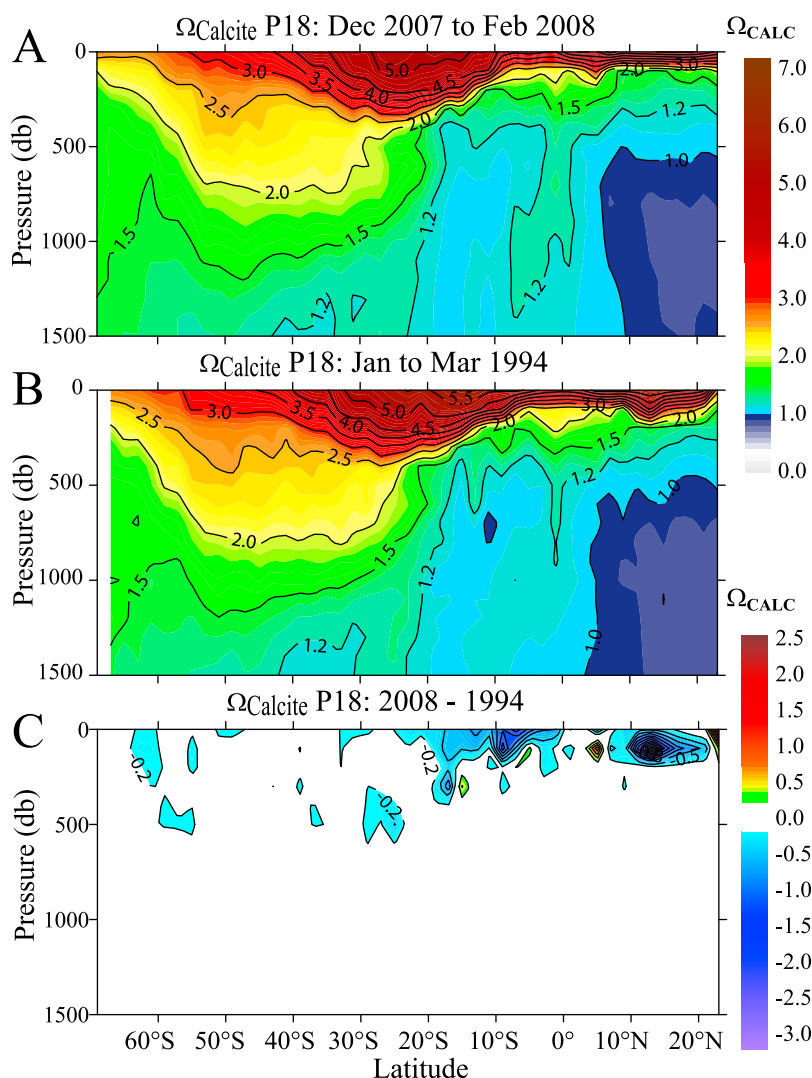
**Figure 6.** Aragonite saturation state for (a) ($\Omega$arag) for 2008, (b) 1994, and (c) $\Omega$arag difference (2008–1994) along the P18 section from Antarctica to Mexico.

because of the higher DIC concentrations relative to TA at shallower depths in the northern hemisphere that result from enhanced upwelling at the equator, at 10°N, and north of about 40°N in the subarctic North Pacific (Figures 2 and 3, respectively). The 2005–06 CLIVAR/CO$_2$ Repeat Hydrography cruise data show a general upward migration of the aragonite saturation horizon of about 1–2 m yr$^{-1}$ along the entire cruise track and an average decrease in the overall aragonite saturation state of about 4.5% in near-surface waters over the 14-year interval between the two cruises. Most of the change in the aragonite saturation state, ranging from +0.3 to −0.5, occurred in the upper 600 m of the water column (Figure 2). The positive changes in saturation state are observed near frontal zones associated with the North Equatorial Current at about 12–14°N where mesoscale changes in salinity and temperature predominate [*Fine et al.*, 2001]. The calcite saturation horizon ($\Omega$cal = 1.0) rose from depths greater than 2800 m in the South Pacific and shoaled to depths less than 200 m between 40°N and 50°N (Figure 3). On average, the calcite saturation horizon in the Pacific shoaled about 1 m yr$^{-1}$ from 1991 to 2006.

### 4.2. The P02 West-East Sections (2004 Versus 1994) in the North Pacific

[10] The west-to-east shoaling of the aragonite and calcite saturation horizons (Figures 4 and 5) is consistent with the shoaling of the TA concentrations shown in *Feely et al.* [2002]. This shoaling is the result of the deep ventilation in the western Pacific and anticyclonic circulation in the North Pacific. The 2004 P02 aragonite saturation horizon ($\Omega$arag = 1.0) shoaled from depths of about 750 m near 140°E to 150 m near 122°W. From there, it deepened slightly to about 300 m near the North American coast. The data indicate a distinct upward migration of the saturation horizon along portions of the section. In particular, for the California Current region between 135°W and 120°W, the saturation horizon in the eastern subtropical Pacific west of the continental shelf has risen more than 100 m since the previous WOCE cruise in 1994. Most of the changes of the saturation state (ranging from +0.5 to −0.5 for aragonite and +0.8 to −0.8 for calcite) occurred in the upper 800 m of the water column, deepening toward the west (Figures 4 and 5). The

**Figure 7.** Calcite saturation state for (a) ($\Omega$cal) for 2008, (b) 1994, and (c) $\Omega$cal difference (2008–1994) along the P18 section from Antarctica to Mexico.

decreases in saturation state occurred between 100 and 600 m and are located in regions where changes in ventilation and uptake of anthropogenic $CO_2$ have major negative impacts on saturation state.

### 4.3. P18 South-North Transects Along 110°W (2007–2008 Versus 1994)

[11] The P18 sections show similar shoaling of the aragonite and calcite saturation horizons from south to north compared with the P16 sections (Figures 6 and 7). The 2007–2008 aragonite saturation depth shoaled from about 1000 m near 40°S to <250 m near 10°S, deepened to ~300 m at the equator, and shoaled to ~150 m near 10°N. The general pattern of aragonite and calcite saturation along the 2007–2008 P18 transect is generally consistent with previous results for 1994 along the same section (Figure 6). The 2007–2008 P18 cruise data show a general upward migration of the aragonite saturation horizon of about 1–2 m yr$^{-1}$ along the cruise track and an average decrease in the overall aragonite saturation state of ~4.5% in near-surface waters over the 14-year period between the two cruises. Most of

the change in the aragonite saturation state, ranging from +0.2 to −0.8, occurred in the upper 500 m of the water column (Figure 6). The calcite saturation horizon rose from depths greater than 2800 m in the South Pacific and shoaled to about 550 m near 10°N in the North Pacific (Figure 7).

### 4.4. The P06 West-East Section (2003) in the South Pacific

[12] The distributions of temperature, salinity, DIC, and aragonite saturation for the P06 west-east 2003 section in the South Pacific are plotted in Figure 8. Since insufficient alkalinity data were collected for the previous WOCE section, it is not possible to make aragonite saturation state comparisons with the earlier data. Nevertheless, this is the first complete east-west aragonite saturation section for the South Pacific. As with the North Pacific, the aragonite saturation horizon shoals from west to east in the South Pacific, starting from depths around 1200 m near 160°W to 800 m near 80°W in the deeper waters. In the eastern South Pacific, there is a large mass of eastward increasing high-DIC, high-salinity, undersaturated water ranging in depths
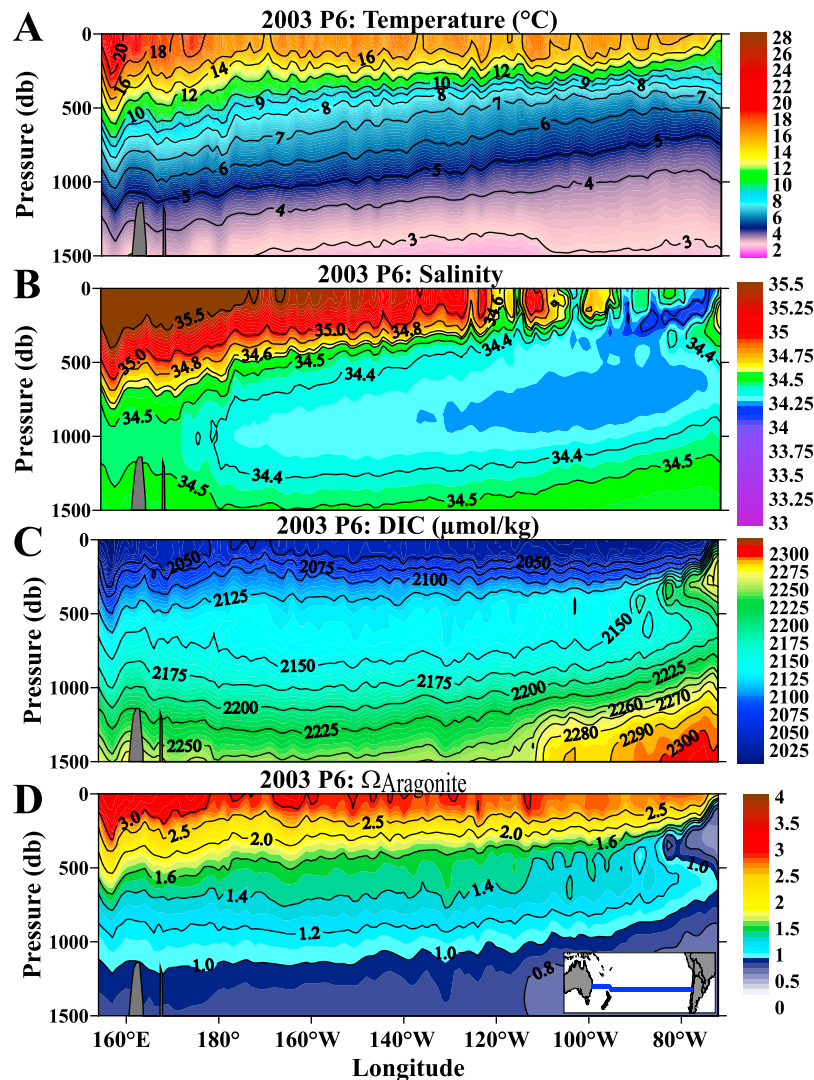
**Figure 8.** West-east distribution of (a) temperature, (b) salinity, (c) DIC, and (d) Ωarag along the P06 Repeat Hydrography section in the South Pacific. The data were collected during the Japanese Repeat Hydrography Section in 2003.

from about 100 to 600 m near the coast of South America. This extremely shallow undersaturated water is probably the result of the uptake of anthropogenic $CO_2$ combined with high amounts of remineralized organic matter along the South American coast, leading to an unusual, heretofore unrecognized, ocean acidification site close to the coast. This site is similar to what has been observed off the west coast of Africa in the South Atlantic [*Chung et al.*, 2003; *Feely et al.*, 2004] and off the west coast of North America [*Feely et al.*, 2008]. In those cases, the oxidation of organic matter augmented by the uptake of anthropogenic $CO_2$ accounted for the observed local reduction in the aragonite saturation state.

### 4.5. Line P

[13] The Line P aragonite and calcite saturation sections for February 2004 are shown in Figures 9a and 9b. At that time the aragonite saturation horizon (Ωarag = 1.0) was shallowest (∼160 m) at the westernmost Station "P" From there, it deepened slightly to about 190 m near the North American coast off Vancouver Island. The calcite

saturation data also suggested a distinct shoaling of the Ωcal = 1 horizon to a depth of about 200 m near station "P" and a gradual deepening of the saturation horizon toward the east. This is consistent with the predominance of downwelling of water properties and carbon system parameters along the coast during the winter months [*Ianson and Allen*, 2002; *Ianson et al.*, 2009]. The shallow depths of the aragonite and calcite saturation horizons occur in regions where uptake of anthropogenic $CO_2$ produces a significant shoaling effect on saturation state (see Section 5 below).

### 5. Discussion

#### 5.1. Estimates of the Relative Role of Anthropogenic $CO_2$ and Circulation Changes on the Vertical Migration of the Aragonite/Calcite Saturation Horizons

[14] The repeat sections allow us to determine the changes in saturation state and upward migration of the saturation horizons over the time intervals of the cruises. These changes can be caused by: 1) uptake of anthropogenic $CO_2$;
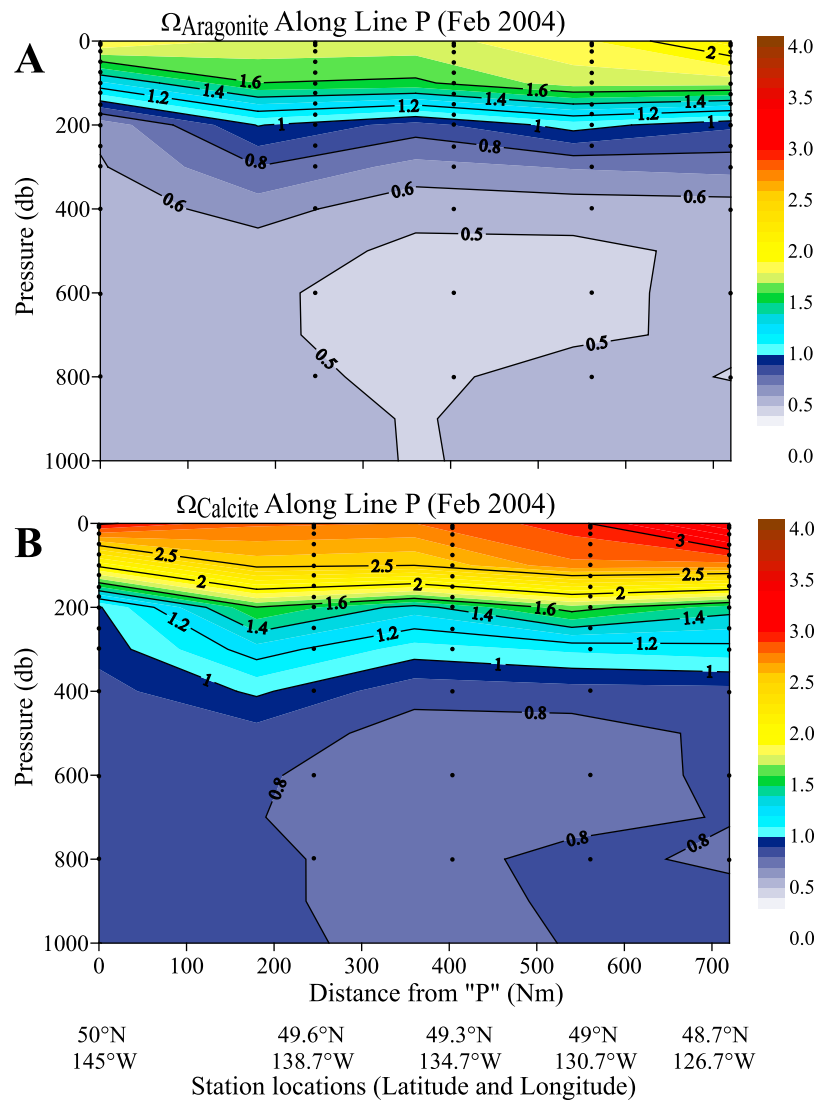
**Figure 9.** Line P sections of (a) aragonite saturation and (b) calcite saturation from Vancouver Island to Ocean Station "Papa" for February 2004.

2) changes in circulation and/or ventilation; and 3) changes in biogeochemical processes. The calculated change in aragonite saturation state between the decadal cruises for each of the transects, which is based on the increase in anthropogenic $CO_2$ as calculated by *Sabine et al.* [2008], is shown in Figure 10. The decrease of the saturation state is regionally variable, with much deeper changes in the South Pacific and western North Pacific than the eastern North Pacific. This is largely due to the fact that the South Pacific and western North Pacific take up more anthropogenic $CO_2$ than the eastern North Pacific [*Sabine et al.*, 2004, 2008]. The situation in the North Pacific is complicated by the fact that in the subpolar North Pacific most of the DIC increase was caused by a decrease in the overturning circulation due to reduced winds since the 1970s, causing an increase in apparent oxygen utilization (AOU) rather than uptake of anthropogenic $CO_2$ [*McPhaden and Zhang*, 2002; *Deutsch et al.*, 2006; *Mecking et al.*, 2008; *Sabine et al.*, 2008; *Sabine and Tanhua*, 2010].

[15] The average shoaling rate of the $\Omega$arag = 1.0 horizon and the average change in saturation state in the upper 100 m due to uptake of anthropogenic $CO_2$ are given in Table 1. The results indicate an upward migration of the aragonite saturation horizon on the order of 1–2 m yr$^{-1}$, with higher shoaling rates in the South Pacific than in the North Pacific because of the higher anthropogenic $CO_2$ uptake in the South Pacific. These rates are roughly consistent with the model estimates for the Pacific Ocean given in *Orr et al.* [2005] for an IPCC IS92a "business as usual" scenario.

[16] The far eastern Pacific data indicate an average upward migration of the aragonite saturation horizon of more than 5 m yr$^{-1}$ in the California Current (Figure 4). This large and unexpected change is primarily due to a significant change in the circulation and water mass properties of the California Current since 1998. A careful analysis of the CalCOFI data [*Di Lorenzo et al.*, 2005] noted large-scale cooling and freshening of the water from 50 to 200 m within the California Current. The authors interpreted these observations
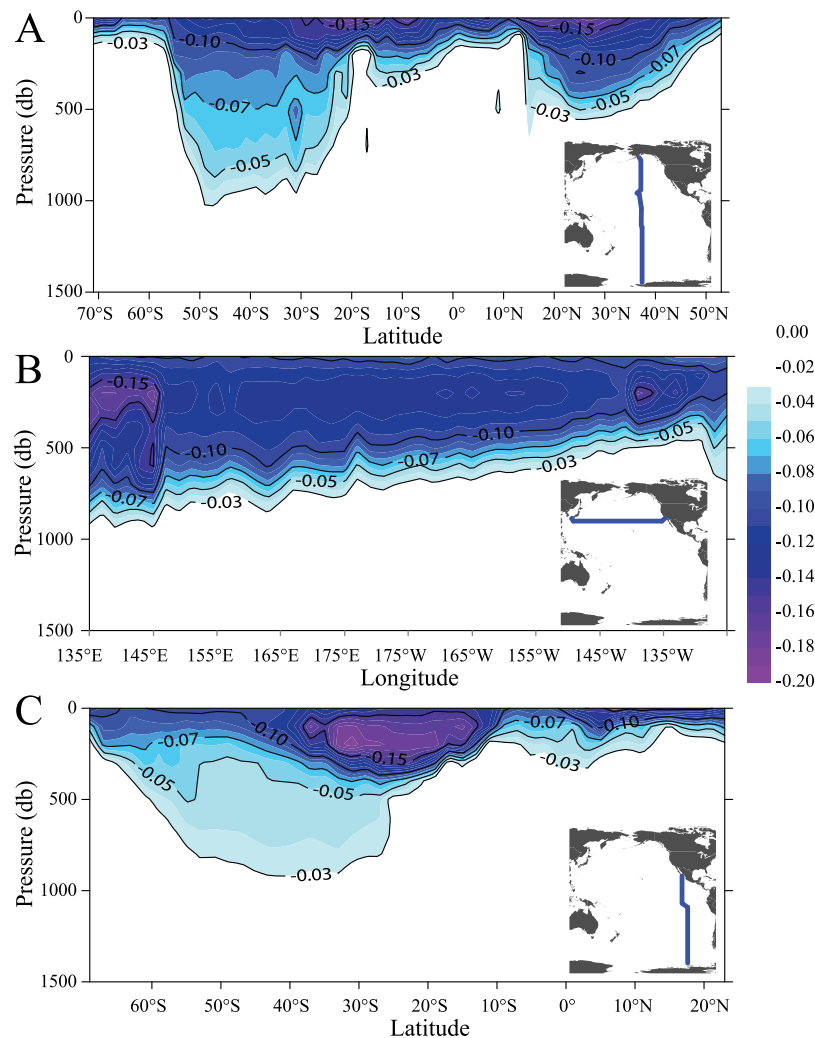
**Figure 10.** Change in aragonite saturation state ($\Omega$arag) along the (a) P16, (b) PO2, and (c) P18 sections based on the anthropogenic $CO_2$ differences from *Sabine et al.* [2008].

as indicating an enhancement of the southward advection of cool, lower-salinity subarctic water coming from the subarctic North Pacific. This interpretation is consistent with our observations of increased amounts of cool, $CO_2$-rich water at the same depths in the 2004 data set compared with the 1994 data. Physical and chemical changes of the water mass properties in the California Current were apparently the major factors controlling the upward migration of the aragonite saturation horizon and probably played a significant role in controlling the seasonal upwelling of corrosive "ocean-acidified" water onto the continental shelf [*Feely et al.*, 2008]. These results suggest that large-scale changes in circulation can be as important as, or in some cases, more important than, the direct effects of anthropogenic $CO_2$ uptake in affecting the location of corrosive water in some parts of the eastern Pacific. More detailed information on the temporal variability of the physical and chemical properties of the California Current is required before we can accurately predict how these long-term changes will affect our coastal ecosystems. In particular, recent modeling of primary production and nitrate transport processes in the California Current ecosystem suggests that increased nitrate supply and

upwelling of lower pH source waters resulting from increased stratification of the North Pacific will cause an enhanced intensification of the acidification in this region over the next century [*Rykaczewski and Dunne*, 2010].

## 5.2. Potential Impacts of the Changes in Aragonite and Calcite Saturation State in the Pacific Ocean

[17] To date, there has been an overall decrease of about 16% in the aragonite saturation state of North and South Pacific surface and intermediate waters since the beginning

**Table 1.** Average Shoaling of the Aragonite Saturation Horizon ($\Omega$arag = 1.0) and Decrease in the Aragonite Saturation State in the Upper 100 m in the South and North Pacific Due to the Uptake of Anthropogenic $CO_2$

| Region | P16 (m yr$^{-1}$) | P18 (m yr$^{-1}$) | P16 $\Omega$arag Decrease (% yr$^{-1}$) | P18 $\Omega$arag Decrease (% yr$^{-1}$) |
|---|---|---|---|---|
| South Pacific | 2.01 ± 0.80 | 1.81 ± 0.85 | 0.34 ± 0.05 | 0.35 ± 0.05 |
| North Pacific | 0.81 ± 0.71[a] | 1.14 ± 0.55 | 0.34 ± 0.07[a] | 0.33 ± 0.01 |

[a]Includes PO2 value at the crossover point.

of the industrial revolution, and a decrease of about 0.34% yr$^{-1}$ over the last two decades (Table 1) [*Feely et al.*, 2004, 2009b; *Caldeira and Wickett*, 2005; *Orr et al.*, 2005; *Kleypas et al.*, 2006]. These rates of decrease are in excellent agreement with those reported by *Ishii et al.* [2011] for the near-surface waters off Japan in the western Pacific. If continued or enhanced over the coming decades, changes in saturation state like this can cause significant changes in overall calcification rates for many species of open-ocean and coastal marine calcifiers including corals, foraminifera, coccolithophores, pteropods, and oyster larvae [*Spero et al.*, 1997; *Bijma et al.*, 1999, 2002; *Kleypas et al.*, 1999a, 1999b; *Marubini and Atkinson*, 1999; *Langdon et al.*, 2000, 2003; *Riebesell et al.*, 2000; *Marubini et al.*, 2001; *Zondervan et al.*, 2001, 2002; *Guinotte et al.*, 2003, 2006; *Reynaud et al.*, 2003; *Sciandra et al.*, 2003; *Seibel and Fabry*, 2003; *Green et al.*, 2004; *Marshall and Clode*, 2004; *Riebesell*, 2004; *Delille et al.*, 2005; *Engel et al.*, 2005; *Langdon and Atkinson*, 2005; *Kleypas et al.*, 2006; *Hoegh-Guldberg et al.*, 2007; *Guinotte and Fabry*, 2008; *De'ath et al.*, 2009; *Hoegh-Guldberg and Bruno*, 2010; *Lischka et al.*, 2011; *Barton et al.*, 2012]. If $CO_2$ emissions continue as projected over the rest of this century, based on the Intergovernmental Panel on Climate Change (IPCC) IS92a $CO_2$ emission scenario ($\sim$800 $\mu$atm $CO_2$ in the year 2100), recent models predict that by the end of this century the surface water DIC could probably increase by more than 12%, and the carbonate ion concentration would decrease by almost 50% [*Orr et al.*, 2005; *Kleypas et al.*, 2006; *McNeil and Matear*, 2006, 2008; *Feely et al.*, 2009b; *Joos et al.*, 2011]. This extent of change in the carbonate species concentrations would cause aragonite undersaturation in all of the Southern Ocean (south of 50°S) sector of the South Pacific and portions of the subarctic North Pacific throughout the entire water column [*Caldeira and Wickett*, 2005; *Orr et al.*, 2005; *Cao and Caldeira*, 2008; *McNeil and Matear*, 2008; *Steinacher et al.*, 2009; *Joos et al.*, 2011]. Throughout the rest of the Pacific, the surface waters would be supersaturated with respect to aragonite and calcite, but the overall saturation state would decrease by as much as 30–40% depending on location [*Cao and Caldeira*, 2008; *Steinacher et al.*, 2009; *Feely et al.*, 2009a; *Joos et al.*, 2011]. These changes would likely be sufficient to cause major changes in calcification rates [*Kleypas et al.*, 1999b; *Hoegh-Guldberg et al.*, 2007; *Hoegh-Guldberg and Bruno*, 2010]. For example, the model output of *Caldeira and Wickett* [2005] predicts a 34% drop in aragonite saturation for a tripling of the pre-industrial $CO_2$ levels by the end of this century. Such a drop in aragonite saturation would cause many coral reef ecosystems to fall well below their normal environmental limit (aragonite saturation $< \sim$3.2) for reef calcification under natural conditions [*Kleypas et al.*, 1999b; *Silverman et al.*, 2009]. For many reefs in the Pacific, changes like these would make calcification unsustainable for corals, possibly compromising the viability of these ecosystems [*Fabricius et al.*, 2011]. Similar decreases in calcification rates would be expected for mussels, clams, and oysters in coastal regions affected by ocean acidification [*Green et al.*, 2004; *Gazeau et al.*, 2007; *Talmage and Gobler*, 2009; *Barton et al.*, 2012]. Other research indicates that many species of shellfish are highly sensitive to higher-than-normal $CO_2$ levels, and that high rates of mortality appear to be directly correlated with the

higher $CO_2$ levels [*Kurihara and Shirayama*, 2004; *Fabry et al.*, 2008; *Guinotte and Fabry*, 2008; *Kurihara*, 2008; *Kroeker et al.*, 2010]. However, it should be noted that aragonite and calcite saturation conditions in coastal waters are more difficult to predict over the long-term because of higher degree of complexity of the physical and biogeochemical processes that cause enhanced localized spatial and temporal variability [*Bates et al.*, 2010; *Andersson et al.*, 2005, 2006; *Feely et al.*, 2008; *Shamberger et al.*, 2011]. Nevertheless, it seems certain that as the levels of dissolved $CO_2$ in seawater rise, the skeletal growth rates of many calcium-secreting species will be reduced in many oceanic regions as a result of the effects of ocean acidification. Thus, if we continue to rapidly increase the $CO_2$ levels in the oceans, there will very likely be direct and profound impacts on marine ecosystems.

## 6. Conclusions

[18] Over the past 250 years, since the beginning of the industrial revolution, there has been about a 16% decrease in aragonite and calcite saturation state in the Pacific Ocean. From repeat oceanographic surveys, we have observed an average 0.34% yr$^{-1}$ decrease in the saturation state of surface seawater with respect to aragonite and calcite over a 14-year period. This has caused an upward migration of the aragonite and calcite saturation horizons toward the ocean surface on the order of 1–2 m yr$^{-1}$. These changes are the result of the uptake of anthropogenic $CO_2$ by the oceans, as well as other smaller scale regional changes in circulation over decadal time scales. If $CO_2$ emissions continue as projected out to the end this century, the resulting changes in the marine carbonate system would mean that many coral reef systems in the Pacific would probably no longer be able to maintain the necessary rate of calcification required to sustain their vitality.

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